



Bis(Benzo-18-crown-6) Derivatives: Synthesis and Ion-Sensing Properties in Plasticized PVC Membranes

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Abstract

Several mono- and bis(benzo-18-crown-6) ethers comprising *o*-nitrophenyl urethane moieties were synthesized and studied as ionophores in PVC membrane electrodes. The bis(crown ether)s were found to exhibit good potentiometric Cs⁺ selectivity over mono and divalent cations as compared to the respective mono(crown ether)s.

Introduction

Crown ethers have been known for more than 40 years and belong to the most effective complexing agents for hard cations, such as alkali metal cations. Complexes of 1:1 crown/M⁺ stoichiometry can be formed if the parameters of the binding site (number of the donor oxygen atoms and the cavity size of the crown ring) fit well the coordination number and the ionic radius of the alkali cation. However, complexes of 2:1 crown/M⁺ stoichiometry can also be formed easily when the cation is larger than the cavity of the crown ether ring. This kind of sandwich complexes are known for 12-crown-4 and Na⁺, 15-crown-5 and K⁺ and 18-crown-6 and Cs⁺ ions. Consequently, the parent mono(crown ether)s can be good extractants but since they do not exhibit sufficient selectivity towards alkali ions, generally their utilization in developing metal ion sensors are of little practical value [1].

Our earlier results [2, 3], in accordance with other studies [4, 5], revealed that bis(benzo-crown ether)s obtained by linking two benzo-crown units via the benzene ring show improved selectivities towards alkali ions as compared to the respective mono-crowns that form 2:1 complexes with the target ions. Numerous bis(benzo-crown ether)s have been synthesized with different linking chains and it was found that bis(benzo-15-crown-5) derivatives **1**, **2**, **3** and **4** (Table 1) exhibit good to excellent K⁺ selectivities over Na⁺ ions in plasticized PVC membrane electrodes. This observation indicates that these ligands preferably bind one potassium ion in the form of an inner sandwich complex rather than two sodium ions separately by the crown units. The superior

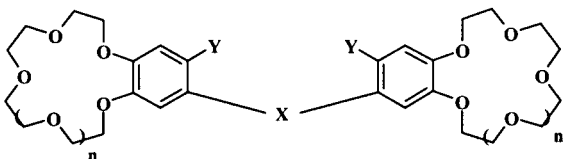
K⁺ selectivities ($\log K_{K^+/Na^+}^{pot} = -3.2$) of ligands **3** and **4** synthesized in our laboratory [2, 3, 6] over ligands **1** and **2** ($\log K_{K^+/Na^+}^{pot} = -2.6$ and -2.0 , respectively) [4, 5] emphasize the importance of the nature of the linkage between the benzene moieties in respect of the preorganization of an appropriate ion trap. Actually, the potassium selective electrode (ISE) based on the highly lipophilic molecule **4** reaches and in some cases exceeds the electroanalytical parameters of the best potassium ISEs based on commercially available ionophores [6]. The enhancement of the selectivity can be due to the *o*-nitrophenyl urethane subunits providing an advantageous preorganizing factor by the formation of intramolecular hydrogen bonds between the nitro and NH groups [6].

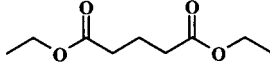
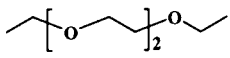
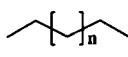
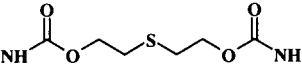
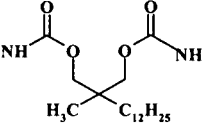
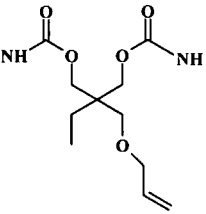
Regarding cesium selective ligands, attempts to demonstrate this “bis(crown ether) effect” with bis(benzo-18-crown-6) derivatives were made by Kimura [7] and others [8, 9]. However, the Cs⁺ selectivity in the presence of K⁺ ions reported for ligands **5** and **6** (Table 1) in plasticized PVC membranes ($\log K_{Cs^+/K^+}^{pot} = -1.09$; and -1.55 , respectively) [7, 8] were comparable with those of several different Cs⁺ selective ligands synthesized recently [10–14] but inferior to some calix[4]arene [15–17] or calix[6]arene [18] compounds (which exhibit $\log K_{Cs^+/K^+}^{pot} = -2.5$ or better), or to a macrocyclic diamine molecule [19].

In this work we attempted to improve the Cs⁺ selectivity of bis(crown ether)s by introducing the advantageous *o*-nitrophenyl urethane structural element into the bis(benzo-18-crown-6) core, and therefore compounds **8**, **9** and **10** were synthesized. Moreover, two mono(benzo-18-crown-6) ethers **18** and **19** were also prepared in order to check the effectiveness of the “bis(crown ether) effect” if it works at

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Table 1. Bis(benzo-18-crown-6) and bis(benzo-15-crown-5) ethers with different linking chains (X) and substituents (Y)



Y	X	Ligand	
		n=1	n=2
H		1	5
H		2	6
H			7
NO ₂		3	8
NO ₂		4	9
NO ₂			10

all with our molecules. The selective ion-binding properties of the ligands were studied in plasticized PVC membranes in the potentiometric operation mode.

Cesium selective electrodes are useful analytical tools for the quantitative determination of radioactive Cs⁺ isotopes in the waste of nuclear power plants, since in current technologies no chemical methods are available for *in-situ* cesium analysis in nuclear waste solutions [20]. Furthermore crown ethers might be potential extractants for the removal of cesium from nuclear waste solutions by solvent extraction [21].

Beside the acceptable Cs⁺/K⁺, Na⁺, Sr²⁺ selectivities, the life time of ISEs and the solid-phase extractant is also of great importance, therefore compound **10** was designed to be immobilized by copolymerisation in a polymer matrix to achieve this goal.

Experimental

Melting points are uncorrected. ¹H NMR spectra were recorded in CDCl₃ at 250 MHz on a Bruker AC 250 instrument using TMS as internal standard. IR spectra were obtained with a Perkin Elmer 1600 FTIR spectrometer. Precoated silica gel plates (Merck 60 F₂₅₄) were used for analytical TLC. All chemicals were reagent grade and used without further purification. Compounds **11** and **12** were prepared as described in the literature [22, 23]. All solutions used were prepared from chemicals of analytical grade and doubly quartz-distilled water.

Synthesis

4'-Acetamido-5'-nitro-(benzo-18-crown-6) (**15**)

4'-Nitro-(benzo-18-crown-6) (**12**) [22, 23] (16.8 g, 47 mmol) was hydrogenated in methanol (300 mL) at atmospheric pressure in the presence of Pd/C (1 g). After filtering off the catalyst, the mother liquor was evaporated to dryness and the crude product (16.2 g, 47 mmol of **13**) was boiled with Ac₂O (6 mL, 63 mmol) in glacial acetic acid (50 mL) for 10 min then the solvent was removed *in vacuum* to afford crude **14** which was used in the next step without isolation. Nitric acid (30 mL, 65%) was added to the mixture of **14** (17.3 g, 47 mmol) dissolved in 200 mL of chloroform and 150 mL of glacial acetic acid at a rate so that the solution temperature did not exceed 20 °C. After stirring for 1 h at room temperature the mixture was poured into crushed ice, the organic layer was washed with water and dried (MgSO₄). The solvent was then removed under reduced pressure and the residue was recrystallized from methanol to give **15** (16.6 g, 85.2%), mp.: 124–125 °C.

4'-Amino-5'-nitro-(benzo-18-crown-6) (**16**)

To 16.6 g (40 mmol) of **15**, 50 mL of 5% aqueous NaOH was added. The mixture was vigorously stirred at 40 °C for 2 h, then for 1 h at room temperature. The separated wet orange crystals were filtered off, dissolved in 200 mL of chloroform and the organic layer dried (Na₂SO₄). After evaporation of the solvent, the residue was triturated with hexane to give crystals (14.4 g, 96.5%), mp.: 123 °C.

4'-Isocyanato-5'-nitro-(benzo-18-crown-6) (**17**)

A chlorobenzene solution (150 mL) of 14.4 g (39 mmol) of **16** was added to 150 mL of chlorobenzene saturated with phosgene at room temperature under stirring and with the introduction of additional phosgene (**Caution! Phosgene is extremely toxic, the reaction should be carried out in a well-ventilated hood only!**). The reaction mixture was then slowly heated to boiling, and when a homogeneous solution was formed, the introduction of phosgene was interrupted. When gas evolution ceased, the excess of phosgene was eliminated with dry argon under boiling (about 1.5–2 h). The solvent was distilled off *in vacuum*, and the residue was washed with hexane furnishing **17** as yellow crystals (13.3 g, 86.3%) mp.: 78 °C.

General procedure for the preparation of crown nitrourethanes 8, 9, 10, 18 and 19

Nitroisocyanate **17** (4.18 g, 10.5 mmol), diol **20**, **21** or **22** (5 mmol) or alcohol **23**, **24** (10 mmol) in 50 mL methylenechloride was allowed to react in the presence of 0.5 mL triethylamine catalyst at ambient temperature overnight. The reaction mixture was subsequently washed with 3% aqueous HCl and water. The organic layer was dried (Na₂SO₄) and the solvent was removed under reduced pressure. The dense yellow oil was dissolved in chloroform and purified by column chromatography in two steps (Brockmann II. neutral Al₂O₃, CHCl₃ eluent; Brockmann II. neutral Al₂O₃, EtOAc eluent) to afford **9**, **10**, **18** and **19** as thick oils. Compound **8** was obtained as a solid, which was purified by dissolving in hot acetone, and precipitated with hexane.

Compound **8**: yellow crystals, (2.26 g, 47%), mp.: 103–104 °C; IR: (KBr): $\nu = 3417 \text{ cm}^{-1}$ (NH), 1736 (CO). ¹H-NMR: 2.85 (t, 4H); 3.5–4.3 (m, 40H); 4.38 (t, 4H); 7.66 (s, 2H); 8.13 (s, 2H); 10.25 (s, 2H). Anal. calcd. for C₃₈H₅₄N₄O₂₀S (918.92); C 49.67; H 5.92; N 6.10; S 3.49; found C 49.50; H 6.04; N 6.14; S 3.54

Compound **9**: yellow oil, (2.05 g, 37%); IR: (KBr): $\nu = 3418 \text{ cm}^{-1}$ (NH), 1736 (CO). ¹H-NMR: 0.89 (t, 3H); 1.25–1.50 (m, 22H); 2.15 (s, 3H); 3.5–4.2 (m, 40H); 4.26 (s, 4H); 7.66 (s, 2H); 8.16 (s, 2H); 10.25 (s, 2H). Anal. calcd. for C₅₀H₇₈N₄O₂₀ (1055.18); C 56.91; H 7.45; N 5.31; found C 56.80; H 7.51; N 5.28.

Compound **10**: yellow oil, (1.73 g, 34%); IR: (KBr): $\nu = 3422 \text{ cm}^{-1}$ (NH), 1737 (CO). ¹H-NMR: 0.95 (t, 3H); 1.57 (q, 2H); 3.42 (s, 2H); 3.5–4.2 (m, 40H); 3.98 (d, 2H); 4.24 (m, 4H); 5.16 (d, 1H); 5.26 (d, 1H); 5.87 (m, 1H); 7.65 (s, 2H); 8.16 (s, 2H); 10.25 (s, 2H). Anal. calcd. for C₄₃H₆₂N₄O₂₁ (970.98); C 53.19; H 6.43; N 5.77; found C 53.31; H 6.30; N 5.82.

Compound **18**: yellow oil, (2.08 g, 41%); IR: (KBr): $\nu = 3424 \text{ cm}^{-1}$ (NH), 1733 (CO). ¹H-NMR: 1.5–1.8 (m, 4H); 3.55–3.80 (m, 12H); 3.85–3.97 (m, 4H); 4.13–4.20 (m, 2H); 4.23–4.30 (m, 2H); 4.44 (t, 2H); 4.85–5.10 (m, 2H); 5.70–5.90 (m, 1H); 7.66 (s, 1H); 8.18 (s, 1H); 10.22 (s, 1H). Anal. calcd. for C₂₂H₃₂N₂O₁₀ (484.50); C 54.54; H 6.66; N 5.78; found C 54.33; H 6.48; N 5.70.

Compound **19**: yellow oil, (2.5 g, 42.9%); IR: (KBr): $\nu = 3420 \text{ cm}^{-1}$ (NH), 1736 (CO). ¹H-NMR: 1.2–2.1 (m, 14H); 3.55–4.35 (m, 22H); 4.85–5.10 (m, 2H); 5.70–5.90 (m, 1H); 7.66 (s, 1H); 8.18 (s, 1H); 10.22 (s, 1H). Anal. calcd. for C₂₇H₄₂N₂O₁₀ (554.64); C 58.47; H 7.63; N 5.05; found C 58.59; H 7.78; N 5.13.

Procedure for the ion-selective measurements

Membrane preparation

5 mg ligand, 65 mg PVC powder (HMW, Fluka 81392), 120 mg plasticizer (*o*-nitrophenyl octylether; *o*-NPOE, Fluka 73732) and as lipophilic anionic sites (additive) potassium tetrakis(*p*-chlorophenyl) borate (KTPCIPB, Fluka 60591, 50 mol% to the ligand) were weighed and dissolved in 1 mL tetrahydrofuran (THF, Fluka 87369, puriss p.a.) and poured into a glass ring (diameter 28 mm) fixed on a glass plate. A

flexible membrane of ca. 0.2 mm thickness remained after the evaporation of THF (ca. 24 h) [24].

Electrodes

Solvent polymeric membranes (diameter 5 mm) were incorporated into conventional ISE electrode bodies (Type IS 561; Philips, Eindhoven, The Netherlands). As an inner electrolyte 10⁻³ M CsCl, while an external reference electrode a double junction Ag/AgCl electrode with 0.1 M Li-acetate salt bridge electrolyte (Radelkis/8201) were used.

Calibration and selectivity measurements

Simultaneous EMF measurements with 6 electrodes were carried out at room temperature using a Radiometer pHM 64 type digital pH-mV meter (Copenhagen, Denmark) coupled to an Orion Model 600 Electrode Switch.

For calibration 10⁻²–10⁻⁷ M cesium chloride solutions were prepared by serial dilution of 10⁻¹ M CsCl stock solution, and the Electromotive Force (EMF) data were measured in each standard solution. The calibration properties of the individual electrodes (slope values (S*) and the detection limits (DL)) were determined from the calibration plot (EMF vs. -log a_{Cs+}). The potentiometric selectivity coefficients were determined by the separate solution method (SSM) [25] from the EMF data measured in 0.1 M chloride solutions of interfering ions (K⁺, NH₄⁺, Na⁺, Pb²⁺, Sr²⁺, Zn²⁺, Ca²⁺, Li⁺, Mg²⁺) and the primary ion, Cs⁺.

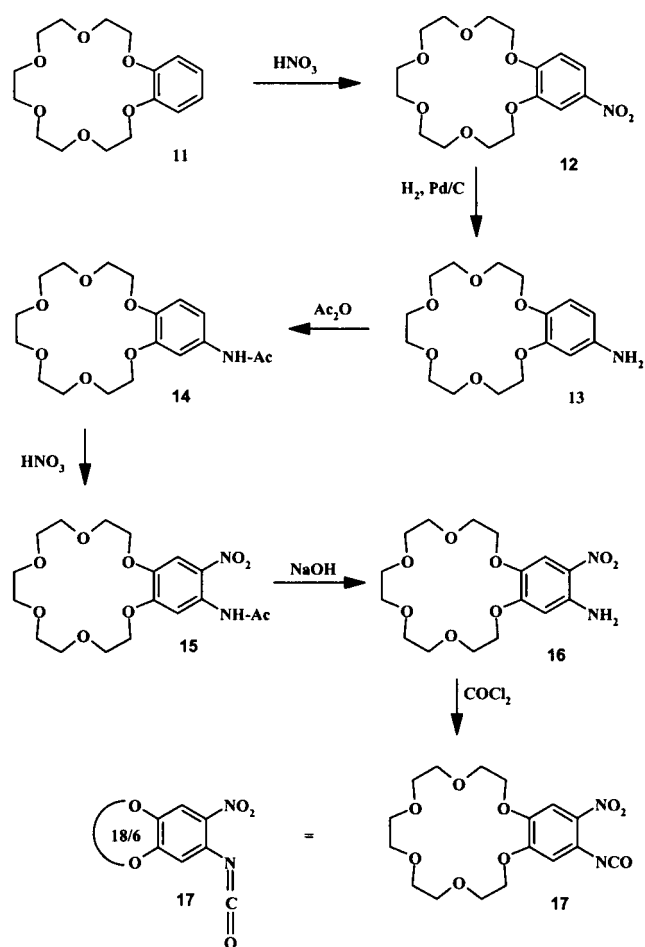
The activity coefficients of the solutions were calculated using the extended Debye–Hückel equation [26], while the liquid junction potential was estimated with the help of the Henderson formalism [26].

Results and discussion

Synthesis

The key intermediate nitroisocyanate **17** was prepared by analogy with the respective benzo-15-crown-5 derivative [2, 3]. Thus, benzo-18-crown-6 (**11**) was nitrated as described in the literature [22, 23] to obtain **12**, which was catalytically hydrogenated at atmospheric pressure and acetylated resulting in the formation of the acetanilide **14**. The subsequent nitration proceeded readily affording **15** regioselectively. The acetyl group was removed with aqueous NaOH followed by action of phosgene on the nitroaniline **16** to obtain **17** in an overall yield of 67% with respect to **11** (Scheme 1).

The synthesis of the target compounds **8**, **9**, **10**, **18** and **19** was straightforward: the reaction of **17** with the respective diols or alcohols (1,5-dihydroxy-3-thiapentane for **8**, 2-methyl-2-dodecyl-1,3-propanediol for **9**, 2-methyl-2-allyloxymethylene-1,3-propane-diol for **10**, 1-penten-5-ol for **18**, and 1-decen-10-ol for **19**) was carried out at room temperature in the presence of triethylamine (TEA) catalyst affording the ligands in good yield after column chromatography (Scheme 2). The structure of the products was proved by ¹H NMR spectra and elemental analysis.



Scheme 1.

Characterization of PVC membranes incorporating ionophores **8**, **9**, **10**, **18** and **19**

The ion selectivity of bis(benzo-18-crown-6) ligand based plasticized PVC membranes was studied potentiometrically by the Separate Solution Method [25] in 0.1 M metal (M^+) chloride solutions. This study revealed that the incorporation of the ligands in plasticized PVC membranes induced excellent cesium selectivity. The selectivity coefficient values obtained by considering cesium ion as a primary ion are shown in Table 2. For comparison the selectivity values obtained for blank membranes (plasticized PVC membranes without ionophore) and for the respective mono-crown ether based membranes (membrane with ligands **18** and **19**) are also listed in Table 2.

The selectivity data ($\log K_{Cs^+/M^+}$) of bis-crowns **8**, **9** and **10** based membranes are rather similar to each other and clearly show that with the exception of $\log K_{Cs^+/K^+}$ a significant improvement is achieved in all selectivity data as compared to that of the relevant mono(crown ether) based membranes. This indicates that the cooperation between the two separate crown rings during ion-binding is likely. However, contrary to our expectations, the Cs^+/K^+ selectivity is hardly improved.

Similarly, comparison of the selectivity properties of ionophore containing and the relevant ionophore free (blank)

Table 2. Potentiometric selectivities ($\log K_{Cs^+/M^+}^{pot}$) of different mono and bis-crown ligands in plasticized PVC membranes and the relevant ionophore free (i.e. Blank) membrane determined by the Separate Solution Method (SSM)*

Ion	Ligand					
	Blank	8	9	10	18	19
Cs^+	0	0	0	0	0	0
K^+	-0.04	-1.37	-1.36	-1.60	+2.04	-0.51
NH_4^+	-0.17	-2.34	-2.15	-2.12	+0.75	-1.91
Na^+	-2.30	-3.3	-3.01	-3.01	-0.04	-2.64
Pb^{2+}	-2.01	-3.87	-3.35	-4.41	-1.3	-2.86
Sr^{2+}	-2.53	-5.1	-5.03	-5.14	-1.02	-3.34
Zn^{2+}	-2.57	-5.40	-5.11	-5.65	-1.05	-3.49
Ca^{2+}	-3.57	-4.88	-5.05	-4.68	-0.92	-3.76
Li^+	-1.82	-5.54	-4.7	-5.38	-0.48	-3.44
Mg^{2+}	-2.36	-6.06	-3.52	-3.80	-0.13	-2.92

*For the calculation of the selectivity coefficient values the theoretical slope values (for monovalent ions 59.16 mV/decade while for divalent ions 29.58 mV/decade at 25 °C) were used.

Table 3. Experimental slope values of the calibration curves (S^*) and the detection limits (DL) of different bis- and mono-crown ligand-based plasticized PVC membranes

Ligand	DL	S^* [mV/decade]
8	6.5×10^{-6}	59.7
9	6.3×10^{-6}	59.6
10	3.2×10^{-6}	55.1
19	5.0×10^{-5}	60.48

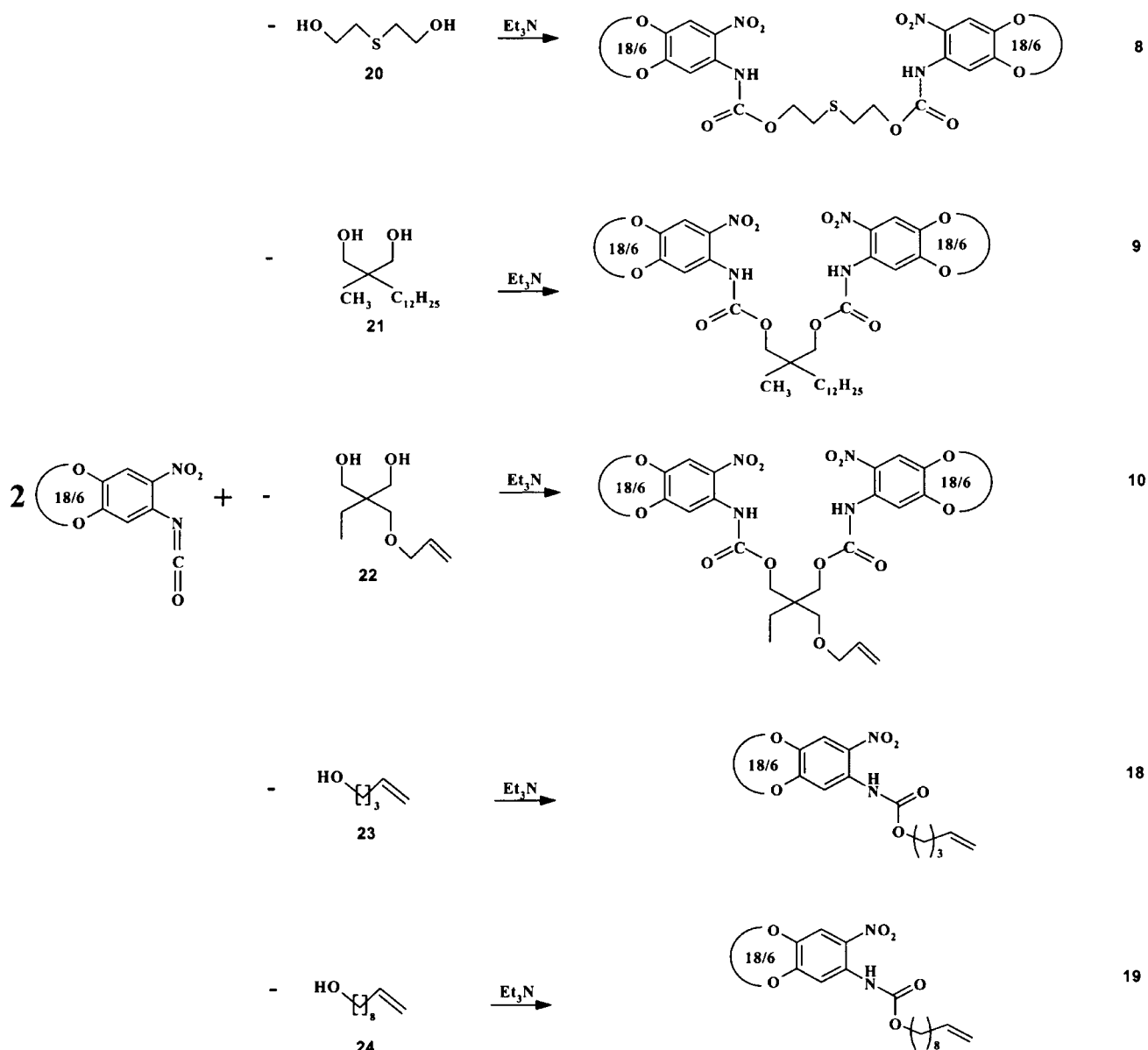
membranes proved that the incorporation of ionophores into the membranes improved ion-selectivity significantly.

It is of interest to note that mono-crowns **18** and **19** differing from each other by the length of the aliphatic substituent, exhibit quite contradictory ion-selectivities. While the ISE made of the former ligand showed good K^+ sensor characteristics, the latter could be regarded as a Cs^+ sensor with poor selectivity ($\log K_{Cs^+/K^+} = -0.51$). For the time being no reasonable explanation has been found for these anomalous experimental data.

The calibration curves of electrodes based on **9** and **10** for Cs^+ in a concentration range of 10^{-1} – 10^{-5} M were found to be strictly linear and the slopes ($S^* = 57$ – 59 mV/decade) clearly demonstrate almost ideal Nernstian responses (Table 3) even in the presence of interfering ions [27]. The detection limits (DL) of **9** and **10** exceed those of other types of bis-crown ethers [4, 5].

The lifetime of the electrodes were also investigated and it was found that the membrane prepared from ligand **8** is not suitable for making an electrode of any practical value. Due to the insufficient lipophilicity, leakage of the ionophore occurred in continuous use within a couple of days resulting in a remarkable decrease of sensitivity and selectivity [27].

In conclusion, it can be stated that we succeeded in the synthesis of Cs^+ selective ligands and prepared cesium sensors based on these ligands with good analytical perform-



Scheme 2.

ances. In respect of Cs^+/Na^+ selectivities ($\log K_{\text{Cs}^+/\text{Na}^+} = -3$) our ligands are superior to some crown-type ionophores ($\log K_{\text{Cs}^+/\text{Na}^+} \approx -2$) [8, 10, 12]. This selectivity coefficient value suggests that the Cs^+ sensor is applicable for Cs^+ analysis in the primary coolant of nuclear plants as it contains primarily Na^+ -ions in excess. Due to the excellent Cs^+ selectivity of the ligands in the presence of Sr^{2+} ($\log K_{\text{Cs}^+/\text{Sr}^{2+}} \approx -5$), further improvements may be achieved in the extraction of radioactive solutions, mainly through immobilizing ligand **10** in different polymer matrices. This work is underway in our laboratory.

Conclusion

Bis(benzo-18-crown-6) derivatives comprising various connecting chains (**8**, **9** and **10**) were synthesized as ionophores for Cs^+ selective liquid membrane electrodes. The most im-

portant electroanalytical parameters of the plasticized PVC membrane electrodes were determined and compared to those published for Cs^+ electrodes based on **5**, **6** and **7** molecules of similar structures. The expected beneficial effect of the nitrophenyl urethane moiety was partly fulfilled: a small increase in the Cs^+/K^+ selectivities but significantly improved selectivities over Na^+ and Sr^{2+} were achieved. These advantages coupled with other excellent electroanalytical performances make some of our ligands promising components of cesium sensors or solid-phase extractants. Moreover, one of the newly synthesized molecules (**10**) has the potential to be immobilized on solid supports.

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